Investigation on the Electrometric Method for Determination of the Chloride.

II. Determination of Chloride in Soils.

By

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In the previous paper, the senior author reported an investigation on the electrometric method for determination of the chloride by using an improved, portable P_H apparatus in conjunction with the method after BEST. This paper deals with the determination of chloride in soils using the method previously described and the results thus obtained are compared with those obtained by the chromate method.

Collection of Samples.

The soil samples were collectted from various points along the irrigation canal which runs from the TAKAHASHI river to the KOJIMA BAY in this prefecture. Some samples were taken from the arable rice-field which are indicated by the arabic figures and the others, from the virgin field located on the bank or basin of the canal and are indicated by the alphabet. This region has a special interest from the standpoint of soil formation since, according to the history, the entire region was under the sea about three hundred years ago, and the present field has been formed ever since and the soil is alluvial naturally. The field is irrigated by the water from the TAKAHASHI river up to the present, and the sea water comes up as far as the water gate indicated on the flood tide and the canal is navigated by the small boats. Consequently the distribution of chloride in the soils along the canal has an intimate interest with farming in this region and also it has a geological interest as well.

Thirty six soils in all, eighteen samples from each the arable and virgin field were collected, dried and ground as usual, and the determinations were carried out as to chlorine by both electrometric and chromate methods, and P_H by the quinhydrone method.

Experimental.

Method of procedure :

Five grams of the soil (ten grams are taken when the chloride content is less than 0.05 per cent.) are placed in a beaker (150 cc.) and fifty cc. of distilled water are added, shaken for a few seconds and allowed to stand for about five minutes. Then the titration is carried out as described previously by adding N/35.46 $AgNO_3$ from the burette until the direction of galvanometer needle is reversed. After each addition, the content of beaker is stirred vigorously, and near the turning point, a few seconds are allowed to complete the reaction. If an excess of $AgNO_3$ is added, titrate back with N/35.46 KCl solution.

The chromate method was carried out as described in the Official Method of Agricultural Chemists (U. S. A.).

The P_H was determined as described in our previous report.

Control titration :

The control determination of chlorine in the standard solution was carried out for both the chromate and electrometric method, and the results are noted in Table I:

Table I.

Control Titration.

KCl Concentration.	cc.	N/35.46 $AgNO_3$.	
		Chromate.	Electrometric.
		cc.	cc.
N/35.46	5.	5.	5.
	10.	10.	10.
N/100	10.	35.	35.
	〃	35.	35.
	〃	35.	35.

N. B. Each datum is the average of three titrations.

Table I indicates that very close results were obtained by both of these method, although the end-point is very much more sharply defined in case of the electrometric method.

Determination of hydrogen ion concentration and moisture content of the soil samples :

The hydrogen ion concentration was determined in view of the fact that in those samples which contain a considerable amount of NaCl, the reaction may be alkaline while the others may be different. The moisture content was determined for ordinary reason. The results are noted in Table II:

Table II.

Hydrogen Ion Concentration and Moisture Content of Soil Samples.

No. of Soils.	p_H	% Moisture content.	No. of Soils.	p_H	% Moisture content.
1.	5.89	4.015	a.	6.76	7.246
2.	6.14	4.828	b.	6.34	5.361
3.	5.92	5.535	c.	6.93	4.642
4.	6.20	3.936	d.	6.78	13.898
5.	5.99	5.091	e.	6.10	5.919
6.	5.67	5.145	f.	6.37	6.115
7.	5.85	3.548	g.	6.98	5.059
8.	6.23	4.025	h.	6.70	4.960
9.	5.27	4.179	i.	5.90	6.728
10.	5.79	4.193	j.	6.50	8.152
11.	5.88	3.442	k.	6.89	4.995
12.	5.72	2.968	l.	6.36	3.523
13.	5.61	2.930	m.	6.25	2.043
14.	5.77	1.861	n.	6.44	0.932
15.	5.82	2.058	o.	6.56	1.044
16.	5.78	2.764	p.	6.56	1.313
17.	5.84	2.632	q.	6.79	0.538
18.	5.96	1.554	r.	6.43	1.991

N. B. The numerical figure indicates the arable soils and the alphabet denote the virgin soils.

As noted in Table II, most of the samples were acid and none alkaline even though some of the samples contained considerable amount of chlorine.

Determination of chlorine in arable and virgin soils :

The samples were treated as described previously, and determination was carried out first by the electrometric method, and the results are noted in Table III :

Table III.

Electrometric Determination of Chlorine in Arable and Virgin Soils.

No. of Soils.	Amount of Sample.	cc. of N/35.46 $AgNO_3$.	% Chlorine.	% NaCl.	No. of Soils.	Amount of Sample.	cc. of N/35.46 $AgNO_3$.	% Chlorine.	% NaCl.
1.	10 g.	3.20	0.320	0.528	a.	5 g.	34.60	6.920	11.409
2.	"	1.50	0.150	0.247	b.	"	17.80	3.560	5.870
3.	"	2.90	0.290	0.478	c.	"	17.90	3.580	5.903
4.	"	0.70	0.070	0.115	d.	"	25.80	5.160	8.508
5.	"	0.90	0.090	0.148	e.	"	8.20	1.640	2.704
6.	"	0.95	0.095	0.157	f.	"	2.30	0.460	0.758
7.	"	0.60	0.060	0.099	g.	"	1.80	0.360	0.594
8.	"	0.55	0.055	0.091	h.	"	1.00	0.200	0.330
9.	"	0.95	0.095	0.157	i.	"	2.20	0.440	0.725
10.	"	0.60	0.060	0.099	j.	"	0.40	0.080	0.132
11.	"	0.35	0.035	0.058	k.	"	0.20	0.040	0.066
12.	"	0.25	0.025	0.041	l.	"	0.10	0.020	0.033
13.	"	0.30	0.030	0.049	m.	10 g.	0.05	0.005	0.008
14.	"	0.20	0 020	0.033	n.	"	0.00	0.000	0.000
15.	"	0.10	0.010	0.016	o.	"	0.00	0.000	0.000
16.	"	0 20	0.020	0.033	p.	"	0.15	0.015	0.025
17.	"	0.30	0.030	0.049	q.	"	0.00	0.000	0.000
18.	"	0.00	0.000	0.000	r.	"	0.10	0.010	0.016

In Table III, the chlorine was transfigured in terms of sodium chloride and along the chlorine. The data indicate that the chloride content decreases gradually toward the source of irrigation water in both the arable and virgin soils. The latter contained much more chloride than the former which indicates that the chloride has been washed out gradually by the irrigation water.

In Table IV, the results obtained by the chromate method are given:

Table IV.

Chromate Method for Determination of Chlorine in Arable and Virgin Soils.

No. of Soils.	Amount of Sample.	cc. of N/35.46 $AgNO_3$.	% Chlorine.	% NaCl.	Nr. of Soils.	Amount of Sample.	cc. of N/35.46 $AgNO_3$.	% Chlorine.	% NaCl.
1.	50 g.	17.2	0.344	0.567	a.	5 g.	34.9	6.980	11.508
2.	"	7.4	0.148	0.244	b.	"	18.4	3.680	6.067
3.	"	14.4	0.288	0.475	c.	"	18.6	3.720	6.133
4.	"	3.6	0.072	0.119	d.	"	26.6	5.320	8.771
5.	"	4.6	0.092	0.152	e.	"	8.2	1.640	2.704
6.	"	4.8	0.096	0.158	f.	"	2.4	0.480	0.791
7.	"	3.2	0.064	0.106	g.	"	1.9	0.380	0.627
8.	"	2.8	0.056	0.092	h.	10 g.	2.3	0.230	0.379
9.	"	4.8	0.096	0.158	i.	"	4.4	0.440	0.725
10.	"	3.2	0.064	0.106	j.	20 g.	1.5	0.075	0.124
11.	"	2.0	0.040	0.066	k.	"	0.8	0.040	0.066
12.	"	1.6	0.032	0.053	l.	15 g.	0.5	0.033	0.054
13.	"	1.8	0.036	0.059	m.	"	0.4	0.027	0.045
14.	"	1.4	0.028	0.046	n.	25 g.	0.3	0.012	0.020
15.	"	1.0	0.020	0.033	o.	20 g.	0.3	0.015	0.025
16.	"	1.2	0.024	0.040	p.	25 g.	0.6	0.024	0.040
17.	"	1.8	0.036	0.059	q.	20 g.	0.3	0.015	0.025
18.	"	0.6	0.012	0.020	r.	25 g.	0.4	0.016	0.026

Table IV indicates approximately the same as in case of Table III.

The data in both tables are condensed in Table V and VI so that their comparison may be made plainly:

Table V.

Comparative Results between Electrometric and Chromate Method.

Nr. of Soils.	% Chlorine.		Diff.	No. of Soils.	% Chlorine.		Diff.
	Electro.	Chromate.			Electro.	Chromate.	
1.	0.320	0.344	—0.024	a.	6.920	6.980	—0.060
2.	0.150	0.148	0.002	b.	3.560	3.680	—0.120
3.	0.290	0.288	0.002	c.	3.580	3.720	—0.140
4.	0.070	0.072	—0.002	d.	5.160	5.320	—0.160
5.	0.090	0.092	—0.002	e.	1.640	1.640	0.000
6.	0.095	0.096	—0.001	f.	0.460	0.480	—0.020
7.	0.060	0.064	—0.004	g.	0.360	0.380	—0.020
8.	0.055	0.056	—0.001	h.	0.200	0.230	—0.030
9.	0.095	0.096	—0.001	i.	0.440	0.440	0.000
10.	0.060	0.064	—0.004	j.	0.080	0.075	0.005
11.	0.035	0.040	—0.005	k.	0.040	0.040	0.000
12.	0.025	0.032	—0.007	l.	0.020	0.033	—0.013
13.	0.030	0.036	—0.006	m.	0.005	0.027	—0.022
14.	0.020	0.028	—0.008	n.	0.000	0.012	—0.012
15.	0.010	0.020	—0.010	o.	0.000	0.015	—0.015
16.	0.020	0.024	—0.004	p.	0.015	0.024	—0.009
17.	0.030	0.036	—0.006	q.	0.000	0.015	—0.015
18.	0.000	0.012	—0.012	r.	0.010	0.016	—0.006

Table VI.

Comparative Results between Electrometric and Chromate Method.

No. of Soils.	% NaCl.		Diff.	No. of Soils.	% NaCl.		Diff.
	Electro.	Chromate.			Electro.	Chromate.	
1.	0.528	0.567	—0.039	a.	11.409	11.508	—0.099
2.	0.247	0.244	0.003	b.	5.870	6.067	—0.197
3.	0.478	0.475	0.003	c	5.903	6.133	—0.230
4.	0.115	0.119	—0.004	d.	8.508	8.771	—0.263
5.	0.148	0.152	—0.004	e.	2.704	2.704	0.000
6.	0.157	0.158	—0.001	f.	0.758	0.791	—0.067
7.	0.099	0.106	—0.007	g.	0.594	0.627	—0.033
8.	0.091	0.092	—0.001	h.	0.330	0.379	—0.049
9.	0.157	0.158	—0.001	i.	0.725	0.725	0.000
10.	0.099	0.106	—0.007	j.	0.132	0.124	0.008
11.	0.058	0.066	—0.008	k.	0.066	0.066	0.000
12.	0.041	0.053	—0.012	l.	0.033	0.054	—0.021
13.	0.049	0.059	—0.010	m.	0.008	0.045	—0.037
14.	0.033	0.046	—0.013	n.	0.000	0.020	—0.020
15.	0.016	0.033	—0.017	o.	0.000	0.025	—0.025
16.	0.033	0.040	—0.007	p.	0.025	0.040	—0.015
17.	0.049	0.059	—0.010	q.	0.000	0.025	—0.025
18.	0.000	0.020	—0.020	r.	0.016	0.026	—0.010

As a whole, fairly close agreements are noted and a majority of cases the chromate method gives higher percentage. It is especially so where the chlorine content is very low.

Influence of organic matter on the amount of chlorine :

Those soils which apparently are rich with organic matter were taken from the samples and were subjected to the shaking for different intervals as noted in Table VI in order to see if any chlorine is held by the organic contents and brought out by shaking :

Table VII.

Influence of Shaking on the Determination.

Time of shaking.	Amount of sample.	No. of Soils.					
		1.	3.	5.	7.	b.	h.
Initial.	5 g.	1.60	1.40	0.50	0.30	17.50	1.00
5 minutes.	〃	1.65	1.45	0.50	0.30	17.40	1.00
1 hour.	〃	1.60	1.45	0.50	0.30	17.40	1.00
5 hours.	〃	1.65	1.50	0.50	0.30	17.40	1.05
24 hours.	〃	1.70	1.40	0.50	0.30	17.30	1.00
Loss on ignition.		10.135	12.369	13.093	10.364	12.548	13.827

Table VII indicates that the amount of organic matter contained as much as in these samples has no appreciable influence on the amount of chlorine by shaking.

Summary and Conclusions.

The following summary and conclusions may be given from this investigation :

1. The method described herein gives satisfactory results in determination of chloride in the soils.

2. The results obtained by the electrometric method are in close agreement with those obtained by the standard chromate method.

3. There is a slight discrepancy among the results when the chloride contents is very low.

4. The chloride content decreases gradually towards the source of irrigation water in both arable and virgin soils.

5. The virgin soils contain much more chloride naturally than the arable soils of which the chloride has been gradually washed away by the irrigation water.

6. The organic matter as much as contained in these samples does not interfere with the determination.